

DEUTERATED WATER HEXAMER OBSERVED BY CHIRPED-PULSE ROTATIONAL SPECTROSCOPY

LUCA EVANGELISTI, CRISTOBAL PEREZ, SIMON LOBSIGER, NATHAN A SEIFERT, DANIEL P. ZALESKI, BROOKS PATE, *Department of Chemistry, The University of Virginia, Charlottesville, VA, USA*; ZBIGNIEW KISIEL, *ON2, Institute of Physics, Polish Academy of Sciences, Warszawa, Poland*; BERHANE TEMELSO, GEORGE C. SHIELDS, *Dean's Office, College of Arts and Sciences, and Department of Chemistry, Bucknell University, Lewisburg, USA*.

The water hexamer is the first cluster size where three dimensional structures become the most stable. For cluster sizes up to the water decamer, the hexamer is unique because there are three low-lying isomers with distinct oxygen framework geometries that can be observed in pulsed molecular beams: the prism, cage, and book. Each structure has a different number of hydrogen bonds (prism: 9, cage: 8, book: 7). The prediction of the lowest energy form by different water potentials has become a benchmark in computational studies of water clusters. The experimental determination that the cage is the lowest energy form was presented by our group in 2012 using the population changes that occur when different carrier gases are used in the molecular beam expansion. Recently, it has been proposed by Babin and Paesani that the relative energy ordering of these isomers might be useful for testing the ability of theory to include zero-point energy effects.^a Their calculations suggested that the prism might become the lowest energy isomer in the fully deuterated water hexamer. At the simplest level, this can be explained by the fact that the prism has the most hydrogen bonds and would, therefore, experience the most energy lowering upon isotopic substitution. Broadband rotational spectroscopy in a pulsed supersonic expansion has been used to study the cage, prism and book isomers of deuterated water hexamer. These data, in conjunction with new computational advances, quantify the changes in the oxygen framework structure respect to the normal water hexamers. Moreover, by using different gases in the expansion we have established that the prism isomer becomes the minimum energy structure as suggested by Babin and Paesani.

^aV. Babin and F. Paesani, "The curious case of the water hexamer: Cage vs. Prism", *Chem. Phys. Lett.* 580, 1-8 (2013).